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Characterization of $BaTiO_3$ Powder Obtained by a Chemical Route

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Abstract

The citric resin method is used to prepare stoichiometric, homogeneous and fine barium titanate powders. The elaboration process is described in detail. Powders are characterized by several methods such as R-ray diffraction, scanning and transmission electron microscopy, thermogravimetric measurements and infra-red absorption and X-photoelectron spectroscopies. Residual carbon content is quantified by nuclear technics and Rosemount method, Raw powders contain small quantities of barium carbonate and residual carbon.

1 Introduction

Today's leading trend in the electronic ceramic industry is to develop component miniaturization. The application of multilayer capacitors implies an increase of the volume efficiency C_v which may be obtained by:

(i) an increase of the relative permittivity ϵ': it may be obtained by grain size control: the dielectric properties are greatly influenced by the grain size; Caboche *et al.*[1] showed that a maximum of ϵ' is observed at room temperature for ceramics having a grain size of about 0·8 μm. The manufacture of such ceramics needs the use of fine powders.
(ii) a decrease of the thickness of the dielectric layers; the production of thin layers again needs fine barium titanate powders.

A wet chemical route to prepare fine and homogeneous powders is interesting compared to conventional solid state reaction processing. In this work, $BaTiO_3$ powders were elaborated by the thermal decomposition of an organic resin produced from a mixed citrate obtained by a method previously described.[2,3] This chemical route allows one to control the Ba/Ti = 1 ratio and the powder morphology and to fix the aggregate size. The Ba/Ti ratio is an important parameter which may dramatically influence microstructural development in high-purity $BaTiO_3$. An excess of BaO involves the formation of Ba_2TiO_4 which inhibits grain growth during sintering and an excess of TiO_2 leads to the formation of an eutectic melt which affects the sintering behaviour because of liquid phase formation at grain boundaries.[4–7]

Different characteristics such as structure, microstructure and residual carbon content must be precise and have been investigated by several methods: transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), infra-red (IR) and X-ray photoelectron (XPS) spectroscopies, nuclear analyses, etc.

2 Experimental Procedure

$BaTiO_3$ powders were obtained from a citric resin method, described in previous papers.[2,3] The mixed citrate $BaTi(C_6H_6O_7)_3,6H_2O$ was first prepared, then dissolved in a citric acid, ethylene glycol and water mixture so that the R = $BaTiO_3$ mass/solution mass ratio was 1%. This solution was calcined at 700°C in static air and $BaTiO_3$ powders were produced after 2 h.

The deagglomeration step was performed in two steps:

(i) first the powder was roughly deagglomerated by attrition: the powder was mixed with ZrO_2 balls in isopropanol in the 1/3 balls, 1/3 isopropanol and 1/3 solid phase ratio and shaken for 12 h.
(ii) the powder was then deagglomerated by ultrasonic dispersion. This step was especially studied. Several factors were investigated, for example sonication time (15–30 min), volume of the suspension (20–50 ml) for a solid weight fraction of 1 g. Optimal condi-

tions were found to be 30 min ultrasonication (100 W power) with 30 ml isopropanol per gram of solid phase. After sedimentation, the suspension was dried in a rotovapor and calcined at 700°C for 4 h before yielding raw $BaTiO_3$ powders.

X-Ray diffraction experiments were performed on a Philips PW 1729 diffractometer with the CuK_α wavelength, at room temperature.

Thermogravimetric measurements were made with a Setaram thermobalance, under a flowing oxygen atmosphere. Approximately 100 mg of powder were accurately weighed in a platinum crucible. The temperature was raised from room temperature up to 1000°C at 10°C min^{-1} and then from 1000 to 1400°C at 5°C min^{-1}.

FT-IR absorption spectra were recorded with a Brucker IFS 113+88 interferometer between 4000 and 400 cm^{-1} at room temperature on a sample containing 2 mg of $BaTiO_3$ dispersed in 200 mg of KBr and pressed into pellets.

Carbon analysis: the carbon concentration was determined by two methods:

(i) the Rosemount carbon analysis consisted of heating a weighted sample by flowing O_2 up to 1800°C and analysing the CO_2 evolved with an infra-red detector. This technique gives the volumic carbon content but is not precise enough at ppm levels.

(ii) the $^{12}C(d,p)^{13}C$ nuclear technique using deuterons from the C.E.R.I.'s[1] van de Graaff accelerator. The method has been described in different articles.[8–11] The measurements were performed at 950 keV deuteron energy in a UHV chamber under a vacuum of about 10^{-9} mbar obtained with a cryogenic pumping system on pellet-shaped samples of 4 mm thickness and 13 mm diameter, isostatically pressed at 250 MPa. The detector was a PIPS silicon diode with 100 mm^2 active surface protected by an aluminium foil of 10 μm thickness, situated 64 mm from the sample position with a $\theta = 150°$ detection angle. The beam current was about 10 nA and the counting time was about 2000 s. A theoretical proton spectrum of a material containing C in the bulk with a C-rich surface layer is given in Fig. 1. It can be seen that the shape of the peak gives information about the C content in the surface layer and in the bulk. In the experimental conditions used, taking account of the differential cross-section[12] and the density of the compacted material (50% of the theoretical density of $BaTiO_3$), the surface layer may be estimated about 0·7 μm and the maximal penetration depth about 1·7 μm. This technique is sensitive down to ppm levels.

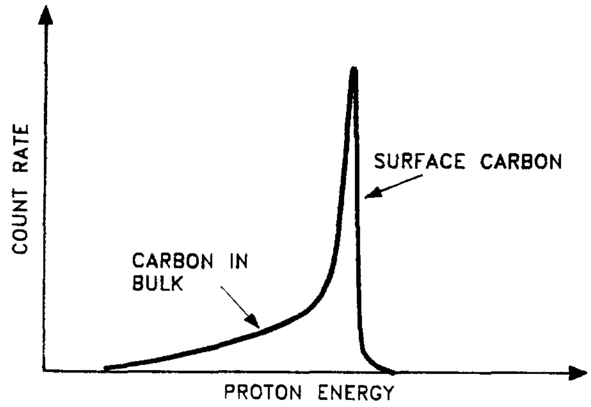

Fig. 1. A theoretical proton spectrum of material containing C with a C-rich surface layer.

X-Ray photoelectron spectroscopy (XPS) analyses were made with an Escalab MK2 of Vacuum Generator system spectrometer using Mg K_α line. The measurements were performed under a vacuum of about 10^{-9} mbar. Samples were obtained by spraying citric precursor on a silica substrate and firing at 700°C. The signal curves were fitted using Gaussian peaks summation and baseline subtraction. Charge compensation was performed using the C_{1s} peak at 284·6 eV.

The SEM images were obtained with a Cambridge stereoscan 100 microscope on samples previously metallized with platinum.

The TEM images were obtained with a JEOL 100 CX microscope on microtomic sections.

3 Results and Discussion

The microstructure is a very important factor which must be controlled during the elaboration of the powder. Figure 2 shows the different agglomeration states of the powder using TEM and SEM techniques. The sample microstructure can be described by (i) microcrystallites of 25–30 nm size (Fig. 2(a)), (ii) crystallites associated into 150 nm spheroid aggregates (Fig. 2(b)) and (iii) aggregates linked in larger agglomerates (platelets about 60 μm in size) (Fig. 2(c)).

Several characterisation methods were used such as XRD, IR absorption and TGA to detect the presence of impurities such as $BaCO_3$. By XRD only one crystalline phase was observed at room temperature, cubic $BaTiO_3$ with cell parameter $a = 4·007$ Å instead of a tetragonal phase as predicted from the phase diagram.[13] This phe-

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[1] C.E.R.I. Centre d'Etude sur les Radiations Ionisantes, CNRS Orléans.

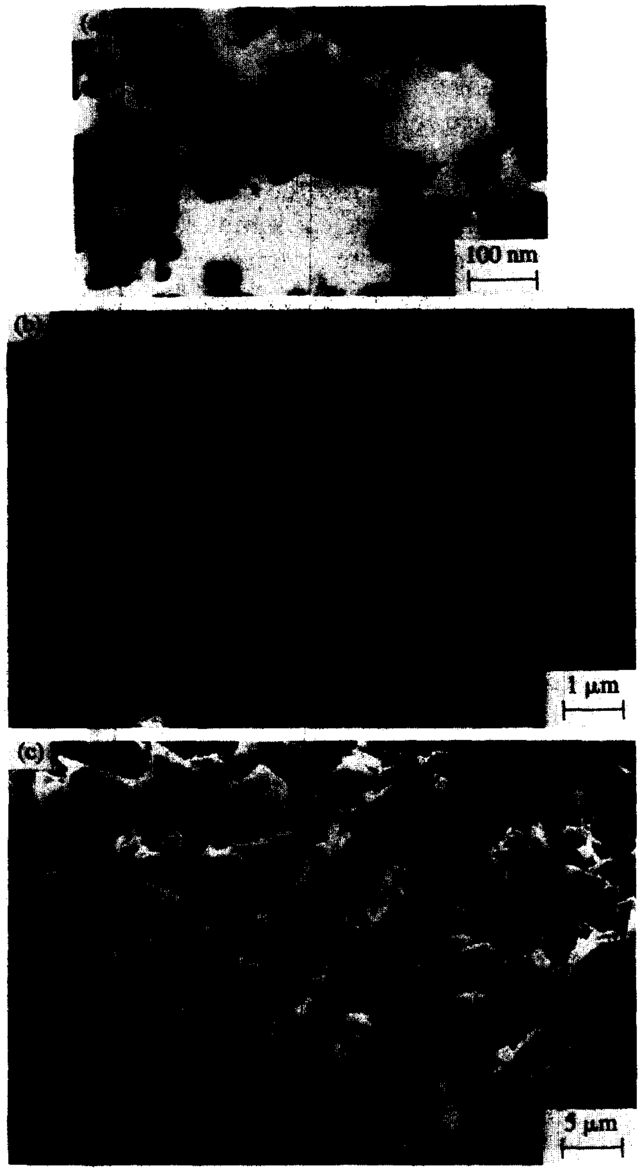

Fig. 2. Microstructure of BaTiO$_3$ powders (a) TEM of ultra-thin sections, (b) SEM of deagglomerated powders, (c) SEM of non deagglomerated powders.

nomenon was already described by Caboche *et al.*[1] They have shown that barium titanate crystallizes at room temperature either in a cubic or a tetragonal phase depending, as well as on cell parameter(s),

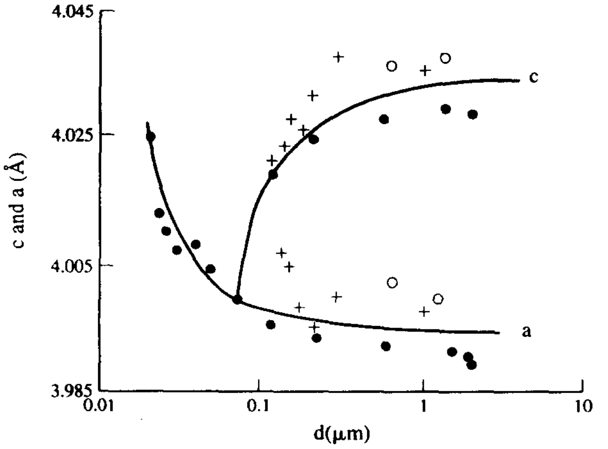

Fig. 3. Variation of cell parameters of fine BaTiO$_3$ powders given by Caboche *et al.*.[7]

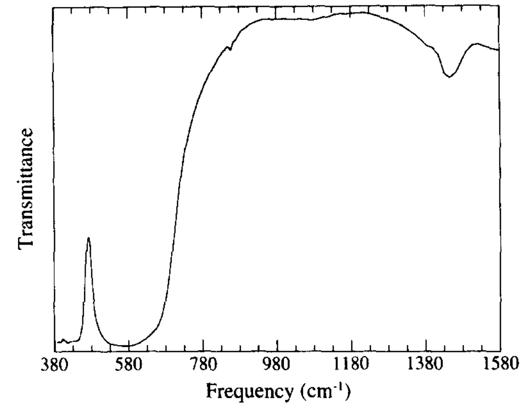

Fig. 4. IR absorption spectra of raw BaTiO$_3$ powders.

on the elementary single crystalline grain size. The cubic cell parameter decreases with this grain size up to a limit of 0·07 μm. Above this limit the crystal cell becomes tetragonal as represented in Fig. 3. Microscopic studies (Fig. 2(a)) have shown that the single crystalline grain size was about 30 nm. According to Caboche *et al.*[1] (see Fig. 3), for such a grain size the powder crystallises in a cubic phase with a cell parameter of about 4·008 Å. Thus, our results are in good agreement with those of Caboche.

The IR absorption spectra recorded at room temperature are presented in Fig. 4 in the 2200–400 cm^{-1} range. The two main absorption bands are characteristic of the vibration frequencies of the TiO$_6$ octahedra. Two other weak absorption bands, at 1430 and 875 cm^{-1}, reveal BaCO$_3$ traces.

These results are in good agreement with those obtained by XPS. The photoelectron peaks of Ba, Ti and O elements were carefully investigated:

(i) the Ti$_{2p}$ line consists of a single narrow Gaussian peak, meaning that titanium was only present in a single chemical state, BaTiO$_3$.
(ii) the study of the 770–800 eV range shows the presence of two barium types (Fig. 5(a)). The two main peaks at 779·5 and 795 eV after calibration of the charge-shifted energy scale can be associated with barium environment in BaTiO$_3$. The third peak at about 785·5 eV can be assigned to barium environment in BaCO$_3$.[14]
(iii) on the oxygen range (Fig. 5(b)) the first peak at 526·5 eV corresponds to the titanate environment and the second one at 527·5 eV may be due to the carbonate.[14] The XPS results confirm the existence of BaCO$_3$ traces.

More quantitative methods were thus necessary to give the residual carbon content in the form of barium carbonate or other carbonaceous species

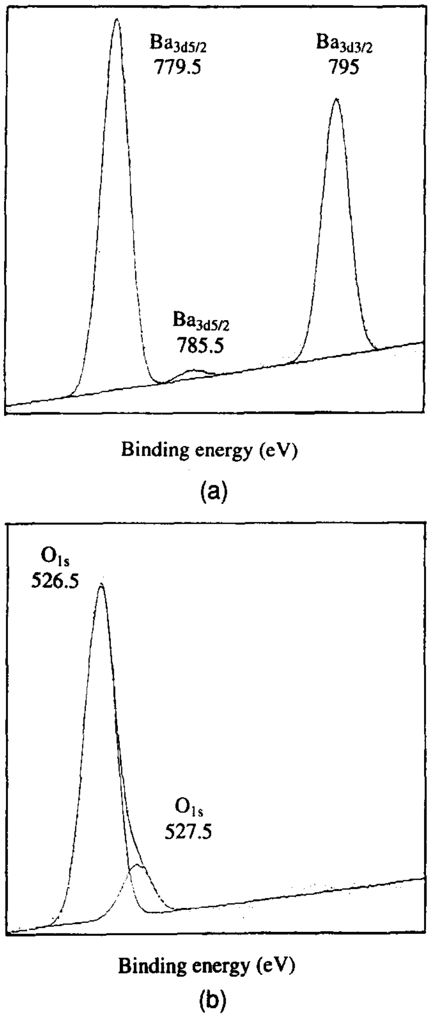

Fig. 5. XPS spectra from raw $BaTiO_3$ powders (a) $Ba_{3d5/2}$ and Ba $_{3d3/2}$, (b) O_{1s}.

more precisely. TGA measurements carried out under flowing oxygen atmosphere gave a curve (Fig. 6) with two weight losses, the first one near 80°C resulting from adsorbed water removal and the second one between 400 and 1100°C which can be due to the CO_2 released during $BaCO_3$ decomposition. Demartin *et al.*[15] and Fang *et al.*[16] have shown that the CO_2 comes mostly from the $BaCO_3$ calcination and that its evolution is observed between 600 and 1300°C on the TGA curves. In our case the corresponding weight loss was estimated about 0·12%.

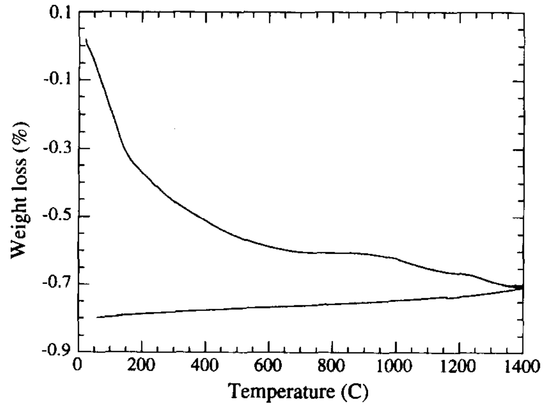

Fig. 6. ATG curve of raw $BaTiO_3$ powders.

The amount of residual carbon in the raw powder determined by the Rosemount method was about 0·25% of the volume.

By nuclear techniques, the carbon content was determined in compacted samples. The surface layer (0·7 μm) of the compacted raw powder exhibits a carbon content of 1·4%. In the volume the C content was estimated at roughly 0·3%.

The results obtained of the volume C content by the two techniques are in very good agreement. The high value of the surface C concentration may be due to the contamination.

If the amount of released CO_2 detected by TGA only originates from the $BaCO_3$ decomposition, we can estimate the $BaCO_3$ concentration at 0·5%. This result is coherent with the XRD results which did not reveal the presence of $BaCO_3$ and the infra-red spectra which displayed two bands of weak intensity assigned to carbonate ions. The carbonate concentration found is low in comparison with those given by different authors for $BaTiO_3$ powders prepared by wet chemical route or hydrothermal synthesis.[14,15,17]

Comparing the results obtained by TGA and carbon content determinations, it can be concluded that the raw powder contains a noticeable residual carbon content in other chemical states than the carbonate one. They could not be found on IR spectra and studies of the XPS C_{1s} peak are now in progress in order to characterize these chemical states.

4 Conclusions

The citric resin method is an interesting way to prepare stoichiometric, homogeneous and fine barium titanate powders. Cubic powders with microcrystallites of 30 nm size were obtained: they contain small quantities of $BaCO_3$ (about 0·5%) which is thermally decomposed between 600 and 1300°C to release CO_2. The total C residual content has been estimated at 00·25–0·30%. Thus a part of the C is in another chemical form than carbonate. Further studies are now in progress to elucidate this point. This synthesis optimization should allow one to obtain dense ceramics with satisfactory bulk capacity.

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